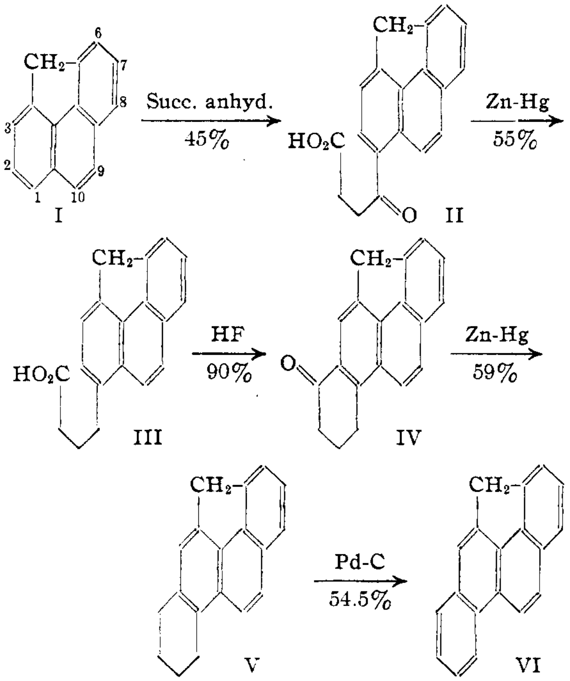
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Synthesis of 4,5-Methylenechrysene and 1',9-Methylene-1,2-benzanthracene from 4,5-Methylenephenanthrene

BY LOUIS F. FIESER AND JAMES CASON[1]

4,5-Methylenephenanthrene (4,5-phenanthrylenemethane) was isolated in small amounts from coal tar by Kruber[2] in 1934 through the sodio and carboxy derivatives but has not as yet been made available by synthesis. We were interested in utilizing the substance as a starting point for the synthesis of higher hydrocarbons of possible carcinogenic activity and also in studying the orientation in a molecule combining special features of both the phenanthrene and the acenaphthene structures. An investigation along these lines has been possible through the courteous coöperation of Dr. O. Kruber, who kindly placed at our disposal a generous supply of the rare hydrocarbon.

In an initial study of the succinoylation of 4,5-methylenephenanthrene (I), it was found that with nitrobenzene and aluminum chloride at 5° there is produced a mixture of keto acids from which one isomer could be isolated in 45% yield and obtained in a completely pure form through the ester. On the basis of evidence to be presented below this substance is assigned the structure of the 1-acid (II). The same product was obtained by succinoylation in the presence of anhydrous hydrogen fluoride[3] but the reaction was less smooth and gave more tar. The reduced acid III was prepared by the Clemmensen reaction and purified by a novel and convenient method consisting in crystallization of the trinitrobenzene derivative and recovery of the acid by extraction with soda solution. By this means satisfactory material was easily obtained starting with partially purified keto acid. After cyclization with hydrogen fluoride[3] to the ketone IV, we tried aluminum isopropylate reduction to the carbinol and treatment with palladium charcoal, but in contrast to Bachmann and Struve's[4] experience with a tertiary carbinol, the results were unpromising. Clemmensen reduction and dehydrogenation proceeded more satisfactorily and gave a highly fluorescent hydrocarbon isomeric with the known 1',9-methylene-1,2-benzanthracene[5] and melting at 172.4–172.9°. The ultraviolet absorption spectrum, which will be reported later by Dr. R. N. Jones, closely resembles those of chrysene and 5-methylchrysene, indicating that the substance is 4,5-methylenechrysene as formulated (VI), and in view of the confirmatory chemical evidence to be presented there can be no doubt on this score. The hydrocarbon bears a certain resemblance to 3,4-benzpyrene in its chrysenoid form[6] and is being assayed for carcinogenicity.



Since the saturation of the 9,10-double bond of phenanthrene leads to homogeneous succinoylation in the 2-position,[7] this expedient was investigated. 9,10-Dihydro-4,5-methylenephenanthrene (VII) was first prepared in this Laboratory by R. C. Clapp and was found to correspond in spectrum to 9,10-dihydrophenanthrene. As with the parent hydrocarbon,[8] hydrogenation over copper chromite catalyst proceeds at a low

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[1] Research Fellow on a grant from the National Cancer Institute.

[2] Kruber, *Ber.*, **67**, 1000 (1934).

[3] Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939).

[4] Bachmann and Struve, *J. Org. Chem.*, **4**, 459 (1939).

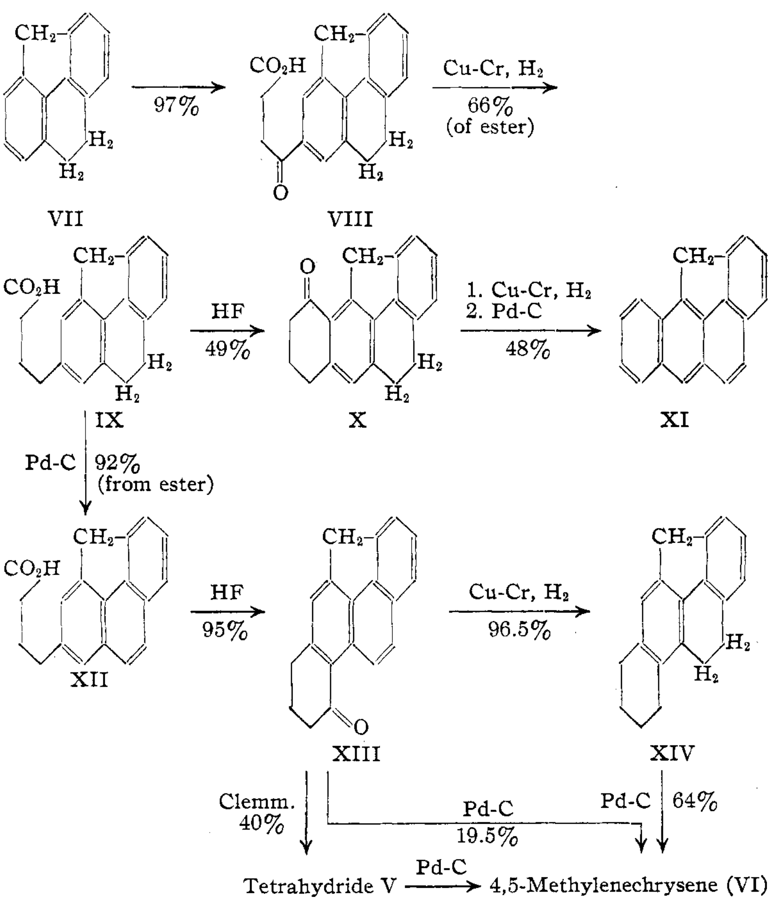
[5] Fieser and Cason, THIS JOURNAL, **61**, 1740 (1939); **62**, 432 (1940).

[6] Fieser and Seligman, *ibid.*, **60**, 170 (1938).

[7] Burger and Mosettig, *ibid.*, **59**, 1302 (1937); Fieser and Johnson, *ibid.*, **61**, 168 (1939).

[8] Burger and Mosettig, *ibid.*, **58**, 1857 (1936); Durland and Adkins, *ibid.*, **59**, 139 (1937); **60**, 1501 (1938).

temperature and affords VII in 85% yield. Succinoylation of the dihydride gave a single keto acid (VIII) in almost quantitative yield and this was reduced most satisfactorily by hydrogenation of an aqueous solution of the sodium salt over copper chromite catalyst. The resulting acid (IX) on cyclization afforded a ketone mixture from which a pure isomer (X) was isolated in only poor yield, and since either the 1- or the 3-isomer could cyclize in only one direction this is an indication that the compound in question is probably the 2-acid (IX). Reduction of the ketone X by high pressure hydrogenation to a hexahydride followed by dehydrogenation, gave an aromatic hydrocarbon identical with the previously described 1′,9-methylene-1,2-benzanthracene[5] (XI), which proves that the dihydro acid (IX) is either the 2- or the 3-isomer. After this dihydro acid had been dehydrogenated in the form of the ester the aromatized acid (XII) underwent cyclization in a different direction, for the resulting ketone (XIII) on reduction and dehydrogenation afforded a fully aromatic hydrocarbon isomeric with 1′,9-methylene-1,2-benzanthracene. If the acidic side chain were located at the 3-position, cyclization could proceed in only one direction regardless of the degree of hydrogenation, and hence the chain must be attached at the alternate 2-position, as in formulas IX and XII. Since ring closure of the aromatized 2-acid XII does not occur in the 3-position, with the formation of a benzanthracene derivative, the reaction must involve the alternate 1-position and give 4,5-methylenechrysene (VI). The product obtained in this series of experiments was identical with that resulting as the end-product in the first series reported, and the chemical evidence of the structure of the hydrocarbon thus coincides with that derived from spectroscopy. A further inference can be drawn from the fact that the aromatized 2-acid XII of the second series is isomeric and not identical with the acid obtained by the succinoylation of 4,5-methylenephenanthrene and reduction. Since this acid gives rise to the 1,2-ring compounds, V and VI, identical with those from the 2-acid, it can only be the 1-acid (III).



The most practical route to the new 4,5-methylenechrysene is that starting with 9,10-dihydro-4,5-methylenephenanthrene and proceeding through VIII, IX, XII, XIII and XIV, and indeed the reactions all proceed so well that the over-all yield in the six-step synthesis from the hydrocarbon isolated from coal tar is 30%. In the next to last stage of this process the reduction of the carbonyl group of the ketone XIII is accomplished very satisfactorily by hydrogenation over copper chromite catalyst, and under the conditions required for effecting this change the 9,10-double bond is likewise attacked and the resulting hydrocarbon is a hexahydride (XIV). 4,5-Methylenechrysene was also obtained directly by heating the ketone XIII with palladium charcoal, as in a comparable case reported by Fieser and Joshel,[9] but the yield was quite poor.

The orientation of 4,5-methylenephenanthrene

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[9] Fieser and Joshel, THIS JOURNAL, 61, 2958 (1939).

in the Friedel and Crafts reaction is quite different from that of the parent hydrocarbon. While phenanthrene is substituted chiefly at the 3-position (50–60%), with the formation of small amounts of the 2-isomers,[10] the 4,5-methylene derivative is attacked chiefly at the 1-position, a difference clearly attributable to the strong para directing influence of the 4-methylene group. This influence is similar to that operative in acenaphthene.

The exclusive 2-substitution of 9,10-dihydro-4,5-methylenephenanthrene parallels exactly the behavior of 9,10-dihydrophenanthrene,[7] the substituent in each case entering an unhindered para position in the diphenyl ring system. The direction of ring closure under the influence of hydrogen fluoride, however, is different in the two series. While γ-(2-phenanthryl)-butyric acid is cyclized largely (78%) in the 3-position,[11] the 2-acid XII undergoes reaction exclusively at the 1-position para to the methylene bridge, and while γ-(9,10-dihydro-2-phenanthryl)-butyric acid is cyclized by hydrogen fluoride solely at position 3,[12] the corresponding acid IX suffers ring closure at the 3-position only to the extent of 49% and evidently much substitution again occurs para to the methylene group. The 4,5-methylene bridge thus constitutes a dominant factor in directing the course of both the inter- and intramolecular acylations of 4,5-methylenephenanthrene.

Experimental Part[13]

β-(4,5-Methylene-1-phenanthroyl)-propionic Acid (II).—A solution of 8 g. of aluminum chloride in 40 cc. of nitrobenzene was cooled in ice and treated with 2.65 g. of powdered succinic anhydride followed by 5 g. of 4,5-methylenephenanthrene, the hydrocarbon being added in half-gram lots with swirling and cooling in ice after each addition. After standing at 5° for seventy-two hours the dark, opaque solution was treated with dilute hydrochloric acid and the solvent was removed with steam. The crude acid, obtained after washing and drying as a brown solid, was treated with Norit in 500 cc. of acetone and crystallized first from 125 cc. of this solvent and then from 150 cc., giving 2.85 g. of almost colorless needles, m. p. 203.5–205° dec. An additional 0.60-g. crop of the same quality was obtained from the mother liquor (total yield 45.4%).

This material consists almost entirely of the 1-acid but contains a trace of isomeric product which could not be separated by direct crystallization. Conversion to the **methyl ester** with diazomethane or methanol–hydrogen chloride gave material melting at 119–122°, and after four crystallizations from benzene–hexane (1:3) the pure 1-ester was obtained as slender, colorless prismatic needles, m. p. 124.8–125.5°. On systematic working of the mother liquors the yield of pure ester was brought to 60%.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.29. Found: C, 78.99; H, 5.46.

On saponification of the pure ester and decoloration of the greenish hydrolyzate with Norit, the free acid crystallized from acetone in the form of colorless blades, m. p. 207–208°, dec.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.61; H, 4.86. Found: C, 78.80; H, 4.91.

Attempts to isolate another isomer by crystallization of the residual material as acid, ester, or salt were unsuccessful. The most nearly homogeneous material melted as the ester at 100–103° and as the acid at 178–184°.

On treating the hydrocarbon (1 g.) and succinic anhydride (0.53 g.) with hydrogen fluoride at room temperature for twenty hours there was recovered from the highly tarry reaction mixture 0.07 g. of the 1-acid, m. p. 203–204.5° dec. (no depression with above product), and very little additional acidic material.

γ-(4,5-Methylene-1-phenanthryl)-butyric Acid (III).—This was prepared most conveniently from the crude keto acid II, purification being accomplished more easily after reduction than before. The use of the methyl ester in the Clemmensen reduction was tried without success, the product being non-distillable. The most satisfactory procedure was essentially that of Martin[14]; a small amount of acetic acid[14] seemed better than a large quantity[4] or than none at all.

One gram of keto acid, m. p. 203.5–205° dec., was refluxed for twenty-four hours with 20 g. of amalgamated zinc, 15 cc. of water, 1 cc. of acetic acid, 20 cc. of toluene and a total of 65 cc. of concentrated hydrochloric acid. The crude acidic material was distilled at 2 mm. and converted in benzene solution into its stable **trinitrobenzene derivative.** Three or four crystallizations of this complex gave satisfactory material, m. p. 183.5–184.5°, whereas the free acid could be obtained pure only after seven to ten crystallizations. The recrystallized analytical sample formed yellow blades, m. p. 183.8–184.8°.

Anal. Calcd. for $C_{25}H_{19}O_8N_3$: N, 8.59. Found: N, 8.82.

By systematically working the mother liquors a total of 1.1 g. of pure trinitrobenzene derivative was obtained. This was dissolved in warm benzene and shaken out with sodium carbonate solution. After washing the carbonate extract three times with benzene the acid was precipitated, dried and crystallized from benzene, when it formed colorless plates, m. p. 176.6–177.6°; yield 0.52 g. (55%).

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.83. Found: C, 82.80; H, 6.00.

4,5-Methylene-7-keto-7,8,9,10-tetrahydrochrysene (IV).—The pure acid III (0.5 g.) was mixed with hydrogen

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[10] Mosettig and van de Kamp, This Journal, **52**, 3704 (1930); Haworth and Mavin, *J. Chem. Soc.*, 1012 (1933).

[11] Fieser and Johnson, This Journal, **61**, 1647 (1939).

[12] Fieser and Johnson, *ibid.*, **62**, 575 (1940).

[13] All melting points are corrected. Microanalyses by Lyon Southworth. The 4,5-methylenephenanthrene employed (total used, 22 g.) was that supplied by Dr. O. Kruber of the Gesellschaft für Teerverwertung and melted at 114.4–115.2°.

[14] Martin, This Journal, **58**, 1438 (1936).

fluoride (20 g.) and after twenty-two hours the residual reagent was largely removed in a stream of air and the residue was shaken with soda solution and benzene. The collected ketone crystallized from alcohol (Norit) as nearly colorless blades, m. p. 167.5–168.5° (0.42 g., 90%). Two further crystallizations gave a sample forming iridescent flat needles, m. p. 168–169°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.53; H, 5.43.

On reducing the ketone with aluminum isopropylate and heating the resulting carbinol for one hour with palladium charcoal at 300–320°, a dark product resulted from which only a small amount of impure 4,5-methylenechrysene could be isolated.

4,5-Methylene-7,8,9,10-tetrahydrochrysene (V). (a) **From the 7-Ketone IV.**—The ketone was reduced by the Clemmensen–Martin method and the product distilled at 2 mm. and crystallized once from alcohol, giving a 59.5% yield of the tetrahydride, m. p. 127.5–128.5°. This did not depress the m. p. of the purified sample described below.

(b) **From the 10-Ketone XIII.**—Following the same procedure, the yield of once crystallized hydrocarbon, m. p. 124–126°, was 40.5%, the lower yield possibly being due to greater hindrance. Six recrystallizations were required to give material of the constant m. p. 129–129.4° (colorless plates).

Anal. Calcd. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.37; H, 6.76.

The dehydrogenation of V is described below.

4,5-Methylene-9,10-dihydrophenanthrene, VII (*with* **R. C. Clapp**).—Fifteen g. of 4,5-methylenephenanthrene was hydrogenated at high pressure over copper chromite catalyst (KAF) at 160° without solvent, one mole of hydrogen being absorbed in about two and one-half hours. The product was separated from catalyst in benzene solution and then treated with Norit in alcohol and crystallized from this solvent. The first crop (12.2 g.) separated as large, colorless plates, m. p. 138–140° and the mother liquor afforded 0.7 g. of satisfactory material (yield 85%). The analytical sample after two more crystallizations from alcohol melted at 140.5–141.2°.

Anal. Calcd. for $C_{15}H_{12}$: C, 93.70; H, 6.30. Found: C, 93.67; H, 6.38.

β - (4,5 - Methylene - 9,10 - dihydro - 2 - phenanthroyl)-propionic Acid (VIII).—The succinoylation was conducted as described for I, using 6.5 g. of the dihydride VII. A solution of the crude acid in warm sodium carbonate solution was clarified with Norit; the precipitated product was light gray and melted at 218–221°, dec.; yield 9.7 g. (99%). Three crystallizations from acetone gave colorless needles, m. p. 224–224.5°, dec.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.07; H, 5.51. Found: C, 77.99; H, 5.66.

It was found most convenient to isolate the acid in the form of the sodium salt as required for hydrogenation to IX. The carbonate solution obtained as above was treated at the boiling point with saturated sodium chloride solution until crystallization commenced, and the salt which separated on cooling was washed with 10% sodium chloride solution and with acetone. After recrystallization in the same manner the yield of almost completely colorless salt was 10 g. (95%).

The **methyl ester,** prepared by Fischer esterification of the crude acid and crystallized three times from methanol, formed colorless needles, m. p. 137.1–137.4°.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.42; H, 5.91. Found: C, 78.51; H, 6.03.

γ - (4,5 - Methylene - 9,10 - dihydro - 2 - phenanthryl)-butyric Acid (IX).—A steel pressure bomb was charged with 7.5 g. of the sodium salt of VIII, 1 g. of copper chromite catalyst, 50 cc. of water, and a few drops of dilute sodium hydroxide. Hydrogenation was conducted at high pressure and 200° until two moles of hydrogen had been absorbed (five to ten hours). The product was extracted with warm water and the solution filtered with Super-cel, then with Norit, and the clear tan filtrate acidified, giving 5.0 g. of crude acid, m. p. 145–149°. Distillation at 2 mm. gave satisfactory material, and the analytical sample obtained by one crystallization from benzene–hexane (1:1) consisted of colorless blades, m. p. 154.5–155°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.00; H, 6.50. Found: C, 81.98; H, 6.70.

Clemmensen–Martin reduction of the keto acid VIII proved less satisfactory, the yield of distilled product being 44%.

The **methyl ester,** prepared by Fischer esterification of the crude acid, was obtained on vacuum distillation as an almost colorless distillate which crystallized immediately on cooling to a solid, m. p. 53–57°; yield 4.6 g. (66% from the keto acid). Four crystallizations from methanol gave colorless plates, m. p. 59.3–60°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.17; H, 6.88. Found: C, 82.15; H, 7.01.

8 - Keto - 1′,9 - methylene - 3,4,5,6,7,8 - hexahydro - 1,2-benzanthracene (X).—Cyclization of 0.5 g. of IX with hydrogen fluoride was conducted as described for the preparation of IV and the crude ketone was treated with Norit in 50 cc. of alcohol and crystallized from 25 cc. of this solvent. There separated 0.35 g. of large, colorless, feathery plates, m. p. 186–197° dec., which on fractional crystallization afforded 80 mg. of X, m. p. 201–203° dec., and 150 mg., m. p. 196–200° dec.; yield 49%. The m. p. of the top fraction was not altered by recrystallization; the fairly broad m. p. range apparently is due to decomposition.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.67; H, 6.19. Found: C, 87.54; H, 6.42.

1′,9 - Methylene - 3,4,5,6,7,8 - hexahydro - 1,2 - benzanthracene was prepared by hydrogenation of 150 mg. of ketone X at high pressure as described below for ketone XIII. Distillation of the crude hydrocarbon gave a nearly colorless crystalline solid, m. p. 78–80°; yield 135 mg. (94.5%). Three crystallizations from alcohol gave 75 mg. of colorless, iridescent blades, m. p. 83–83.5°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.65; H, 7.35. Found: C, 92.78; H, 7.71.

1′,9-Methylene-1,2-benzanthracene (XI).—The mother liquors from the crystallization of the above hexahydride were evaporated to dryness and the residue, together with 50 mg. of pure material, was heated with 15 mg. of palladium charcoal for thirty minutes each at 220–265° and at 265–300° and finally for ten minutes at 300–320°.

After distillation, the pinkish material was converted to the picrate and this was crystallized twice from alcohol in the presence of excess picric acid and then decomposed by passage in benzene through a tower of alumina and Super-cel. Crystallization from alcohol then gave 50 mg. of 1′,9-methylene-1,2-benzanthracene, m. p. 120–121°, which formed a brilliant orange trinitrobenzene derivative, m. p. 161.5–162°. These two substances gave no depression when mixed with authentic samples.[5]

γ-(4,5-Methylene-2-phenanthryl)-butyric Acid (XII).—A mixture of 5.25 g. of the distilled methyl ester of γ-(4,5-methylene-9,10-dihydro-2-phenanthryl)-butyric acid (IX) and 0.60 g. of palladium charcoal was heated at 200–240° for thirty minutes, at 240–250° for thirty minutes, and at 250–265° for thirty-five minutes. The catalyst was removed by filtering a solution of the product in benzene and the ester was distilled at 2 mm., giving 5.05 g. of colorless distillate which soon solidified, m. p. 32.5–34.5°. A sample of this **methyl ester** when crystallized twice from methanol formed colorless, iridescent plates, m. p. 36.3–37.3°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.74; H, 6.23. Found: C, 82.81; H, 6.56.

For saponification the ester was refluxed for forty-five minutes with 25 cc. of 1 *N* alcoholic potassium hydroxide and the solution was poured into 500 cc. of water (clear solution) and acidified. The light tan precipitated product (4.7 g., m. p. 164–166°) was clarified in benzene and crystallized from 75 cc. of benzene and 50 cc. of hexane. After collecting a first crop of 4.4 g. of plates, m. p. 167–167.6°, the mother liquor afforded material which after two recrystallizations melted at 164-165.5° (0.10 g.); total yield 92%, from the dihydro ester. A sample crystallized twice more from benzene–hexane formed colorless blades and plates, m. p. 167.7–168.0°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.83. Found: C, 82.84; H, 6.10.

10 - Keto - 4,5 - methylene - 7,8,9,10 - tetrahydrochrysene (XIII).—Cyclization of 4.4 g. of the acid XII was conducted in hydrogen fluoride (120 g.) for sixteen hours and the product was isolated as described for the isomeric ketone IV, giving 3.70 g. of pale yellow plates, m. p. 171.5–173°, and 0.19 g., m. p. 169.5–171°; yield 95%. Two more crystallizations from alcohol gave highly iridescent plates with a yellowish reflex, m. p. 173–174°.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.18; H, 5.69.

4,5 - Methylene - 7,8,9,10,11,12 - hexahydrochrysene (XIV).—One gram of the 10-ketone XIII in 7 cc. of absolute alcohol was hydrogenated at 160° under high pressure in the presence of 0.10 g. of copper chromite catalyst. The reaction proceeded rapidly and in less than one hour three moles of hydrogen had been absorbed; the absorption then became quite slow and the reaction was stopped. Distillation of the collected product gave 0.92 g. (96.5%) of almost colorless material which softened at 105° and melted at 110–115°. After three crystallizations from alcohol, the hydrocarbon formed clusters of colorless blades, m. p. 116.6–117.2°.

Anal. Calcd. for $C_{19}H_{16}$: C, 92.65; H 7.35. Found: C, 92.63; H, 7.52.

4,5-Methylenechrysene (VI). (a) From the Hexahydride XIV.—The hexahydride (920 mg.) was heated with palladium charcoal (100 mg.) in a bath initially at 220°. The temperature was gradually raised to 265° in the course of one hour and held at 265–270° for fifty minutes. After separation from the catalyst the hydrocarbon was conveniently isolated as the trinitrobenzene derivative. Two crystallizations from alcohol gave 1.21 g. of complex, m. p. 193.5–194.5°, which was decomposed by reduction with stannous chloride. An initial crystallization of the recovered hydrocarbon from alcohol gave 480 mg., m. p. 172.4–172.9°, and 90 mg., m. p. 170–170.8°; total yield 64%. The compound crystallizes in highly iridescent colorless plates, many of them diamond shaped. Both the solid and its solutions show a violet fluorescence in daylight and give a particularly intense violet in ultraviolet light.

Anal. Calcd. for $C_{19}H_{12}$: C, 94.96; H, 5.04. Found: C, 95.10; H, 5.09.

The **trinitrobenzene derivative** crystallizes from alcohol in bright orange needles, m. p. 194–195°.

Anal. Calcd. for $C_{25}H_{15}O_6N_3$: N, 9.27. Found: N, 9.08.

The **picrate** forms bright red, flat needles from alcohol but is rather unstable.

(b) From the Tetrahydride V.—Dehydrogenation of 150 mg. of V with 20 mg. of palladium charcoal at 250–265° for one hour gave, after distillation of the product and crystallization from alcohol, 45 mg. of VI, m. p. 171.5–172.3°, and 12 mg., m. p. 169–170.2° (54.5%, no depression with above sample).

(c) From the 10-Ketone XIII.—A sealed Pyrex tube containing 200 mg. of XIII and 25 mg. of palladium charcoal was heated at 275–285° for six hours. (The yield was slightly lower on heating at 315° for three hours or at 265° for two hours.) The material was dissolved in benzene and the filtered solution passed through a column of alumina and Super-cel (1:1). In ultraviolet light the filtrate was brilliantly fluorescent and a yellow zone appeared at the top of the column, followed by a blue zone. The product recovered from the filtrate on distillation at 2 mm. gave 80 mg. of colorless crystalline distillate. Two crystallizations from alcohol afforded 45 mg. of hydrocarbon, m. p. 167–168.5°, which was combined with similar material from other runs and recrystallized four times. By systematic working of the mother liquors, with use of the trinitrobenzene derivative, there was obtained in all a 19.5% yield of pure 4,5-methylenechrysene, m. p. 172–172.5°, which gave no depression when mixed with the above samples.

Summary

By the Friedel and Crafts condensation of 4,5-methylenephenanthrene with succinic anhydride the 1-keto acid is obtained in 45% yield and affords a suitable intermediate for the synthesis of the new 4,5-methylenechrysene. 9,10-Dihydro-4,5-methylenephenanthrene undergoes succinoylation exclusively in the 2-position, and after reduction ring closure can be effected at the 3-position, providing in moderate yield a ketone

which can be converted into the known 1′,9-methylene-1,2-benzanthracene. γ-(4,5-Methylene-2-phenanthryl)-butyric acid is obtained in good yield by dehydrogenating the dihydro intermediate as the ester and it cyclizes exclusively at position 1, affording a very satisfactory route to 4,5-methylenechrysene in which the over-all yield from 4,5-methylenephenanthrene is 30%.

The structures of the different products are fully established by the transformations indicated. In all of the inter- and intramolecular acylations observed in the 4,5-methylenephenanthrene series a strong para directive influence of the 4-methylene group is discerned.

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Certain Trialkylated Benzenes and their Compounds with Aluminum Chloride and with Aluminum Bromide

BY JAMES F. NORRIS AND JOHN N. INGRAHAM[1]

In a recent paper[2] methods were described for the preparation, with high yields, of mesitylene and *s*-triethylbenzene by the Friedel–Crafts reaction. By the use of similar conditions toluene and *m*-xylene were ethylated and methyldiethyl- and dimethylethylbenzene were prepared. It seemed highly probable that these hydrocarbons had the symmetrical structure, although the properties of some of their derivatives were not in accord with those recorded in the literature for the symmetrical hydrocarbons.[3]

The ethyldimethylbenzene has been restudied and additional evidence is presented in favor of the symmetrical structure of the hydrocarbon.

In the paper by Norris and Rubinstein results were given of the study of the product formed from toluene, aluminum bromide and hydrogen bromide. Since Gustavson[4] has reported that the compound containing *s*-triethylbenzene and aluminum bromide is a crystalline solid, the investigation of this substance was undertaken. It was formed by passing hydrogen bromide into a solution of aluminum bromide in the hydrocarbon. Heat was generated and a light red oil separated from the excess of hydrocarbon. When cooled the compound formed yellow crystals which melted at 64–66°. Analyses of the crystals gave results which checked with the formula proposed by Gustavson: $Al_2Br_6 \cdot 2C_6H_5(C_2H_5)_3 \cdot HBr$. The complex was held at 0.002 mm. pressure at room temperature. When it came to constant weight the residue was shown by analysis to contain the Al_2Br_6 and hydrocarbon in the ratio of 1 to 1.

When the crystalline complex was treated with acetyl chloride, the yield of methyltriethylphenyl ketone was 67%.

An attempt was made to prepare a compound having the formula $Al_2Br_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HCl$ by passing hydrogen chloride into a solution of the bromide in the hydrocarbon. Analyses of the product from time to time showed that the bromine in aluminum bromide was being replaced by chlorine. When aluminum chloride and the hydrocarbon were treated with hydrogen bromide, the chlorine was replaced and the complex containing aluminum bromide was formed.

A crystalline complex having the formula $Al_2Cl_6 \cdot 2C_6H_3(C_2H_5)_3 \cdot HCl$ was isolated. The complex prepared from mesitylene had the formula $Al_2Br_6 \cdot 3C_6H_3(CH_3)_3 \cdot HBr$ (m. p. 47–48°). When held at 0.002 mm. to constant weight the residue contained Al_2Br_6 and $C_6H_3(CH_3)_3$ in the molecular ratio 1:1.

The complex with pseudocumene contained three moles of hydrocarbon. The complex with benzene and aluminum bromide was very unstable. When held at 12 mm. pressure, nearly all the benzene was lost.

The complex prepared from toluene and aluminum bromide when held at 12 mm. to constant weight left a residue which contained one mole of the hydrocarbon to one of Al_2Br_6. When held at 0.002 mm., it lost nearly all the hydrocarbon. The compounds containing trimethyl and triethyl benzene (ratio to Al_2Br_6 1:1) were stable at this

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[1] From a part of the thesis of John N. Ingraham submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1938.

[2] Norris and Rubinstein, THIS JOURNAL, **61**, 1163 (1939).

[3] Jacobson, *Ber.*, **7**, 1430 (1874); Tohl and Geyger, *ibid.*, **25**, 1533 (1895).

[4] Gustavson, *Compt. rend.*, **140**, 940 (1905).